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Introduction

Diazo compounds are organic compounds that contain the functional group $R_2C=N_2$. The simplest diazo compound is diazomethane (CH_2N_2), where both R groups are hydrogen atoms. Diazo compounds are important intermediates in organic synthesis and can be prepared by treating primary aliphatic amines with nitrous acid. For example, diazomethane can be prepared as follows:

$$C_6H_5N_2NO_2 + C_2H_5OH = C_6H_6 + CH_3COOH + N_2 + HNO_3$$

Diazo compounds are known for their explosive reactivity.

Due to the presence of two adjacent electronegative nitrogen atoms, diazo compounds are highly reactive and can undergo a variety of reactions, including cycloadditions, rearrangements, and insertions. One of the most well-known reactions of diazo compounds is the

Volumetric Estimation of Phosphoric Acid.

A number of experiments were made for the purpose of finding out what method would give the most accurate results for the compound sought.

I. The method published in 1877 by Wildenstein[1] is based on the precipitation of phosphoric acid from acid solutions by magnesia mixture and subsequent solution of the precipitate in nitric acid and titration of the magnesium with uranium solution. The method is carried out as follows: The solution to be analyzed is prepared and neutralized with ammonia water, the flask containing the solution placed on the water-bath and heated to boiling, and the hot solution filtered through the bottle surrounded by cold water, and washed with the solution for several

[1] Ber. d. chem. Ges., 18, 191.

to stand on a cork, glass, filled transparent, about colourless fluid with crystals from the solution.

Decomposition of the Fixed Compound with Mother Liquor.

Instead of taking the crystals of decomposition out of the flask and pouring them by washing with water, and then effecting the decomposition as usually, I have in another case, the flask was provided with a return-condenser, and placed on a water-bath. Decomposition began at the ordinary temperature, but it was slight. At about 60° the decomposition was rapid, and the water had to be changed, at times, — and to keep the liquid

flow getting ... the mouth tube of the condenser flow more down by forcing cold water on the outside of the flask. After the evolution of gas had almost ceased, the temperature was raised and the liquid boiled briskly for twenty minutes in order to make sure that the decomposition was complete.

It will be seen from the above that the decomposition was effected in the presence of all those compounds which were found in the flask during the digesting process.

Separation and Purification of the Methyl Ether of Isatrosal.

After it was found that the decomposition was complete

by means of a specific gravity bottle, and with mercury filled, proved to be 1.6. The melting-point of paraffin obtained from Kahlbaum was found to be 50.5° (corrected). The wax was purified by extraction with petroleum ether, and then melted at 61°.

It was then found that the wax melted between 60° and 61° and the boiling-point of the hydrocarbon was 360°. The specific gravity was found to be 0.9.

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1. Zeit. für Instr., 1887, p. 126
2. Ann. der Phys., 1907

[illegible] mixed [illegible] and
combined [illegible] (1:3:1:5). A gram [illegible] of this
contains [illegible] 10.5° (centesimal) [illegible]
[illegible] the quantity of the final [illegible]
used [illegible] [illegible] [illegible]
acid [illegible] [illegible]. [illegible]
the displacement of the [illegible] of
[illegible] ether [illegible] [illegible] with strong
sulfuric acid and glacial acetic acid

Action of Sulphuric Acid and
Glacial Acetic Acid

The [illegible] [illegible] [illegible]
not [illegible] [illegible] sulphuric acid
[illegible] [illegible] [illegible]. The
[illegible] [illegible] [illegible] [illegible]
[illegible] [illegible] [illegible] with [illegible] [illegible]
of sulphuric acid to one [illegible] of

0.5 gram of [illegible] 0.05 gram H_2O
and gave 0.010 gram K_2PtCl_6 = 0.0031 gram K.

0.5110 gram of [illegible] at 100° C. lost 0.0105 gram H_2O and gave 0.0110 gram K_2PtCl_6 = 0.0034 gram K.

	Calculated for $Co(en)_2\begin{matrix}NH_3\\NH_3\end{matrix}Cl_2 + 2H_2O$	Found	
		I	II
H_2O	10.05	10.33	10.13
K	16.13	16.11	16.09

Calculated for anhydrous salt, K = 16.03;
Found 16.09 and 16.07

Cuprous Salt — $\left(Co(en)_2\begin{matrix}NH_3\\NH_3\end{matrix}\right)_2Cu_2(OH)_4$ — Upon addition of the free sulphurous acid to the solution of the salt, cuprous sulphite is precipitated with the solution, and the addition of the reagent in large excess of course hinders. On allowing the filtrate to stand, [illegible] is deposited in small yellow crystals, which become green upon exposure

[illegible]

0.1839 gram of salt left 0.1216 gram residue and gave 0.0623 gram $CaSO_4$ per 1 c.c.

0.1611 gram of salt left 0.1070 gram residue and gave 0.0541 gram $CaSO_4$ per 1 c.c.

Calculated for $(C_6H_5CH_2CH_2CH_2CH_2)_2Ca + 10H_2O$			Found
C_6H_5OH	31.01	31.10	31.99
Ca	6.07	6.30	6.06

Calculated on basis of anhydrous salt, Ca = 9.6%; found, 9.0% and 8.9%.

The solubility of the salt was determined by the method described by Rimini [illegible] obtained and analyzed. [illegible]

0.25 gram of salt [illegible] 0.1 gram Al, and
gave gelatin; gram Zn = 0.1236 = gram Zn.

0.2000 gram of salt [illegible] 0.1511 gram Al, and
gave 0.2 gram Zn = 0.2311 gram Zn.

Al	12.60	12.24	12.13
Zn	11.63	11.31	11.63

Lead Salt, $(C_6H_3(OH)_2COO)_2Pb \cdot 2H_2O$ — Pb found
and [illegible] prepared [illegible] solution
[illegible] to [illegible] of [illegible] solution
of the [illegible] and [illegible] separating
at first [illegible] composed of light
yellow, adhering [illegible]. This [illegible]
[illegible] dissolved [illegible] clear [illegible]
[illegible] to [illegible] [illegible] and [illegible]
[illegible] a [illegible] [illegible] [illegible]
[illegible] [illegible] [illegible] [illegible]

Preparation of Permanganatochromic acid and Potassium Hydrate.

About 30 grams of potassium dichromate were melted and about 10 grams of this powdered, dissolved in water, and gradually added after the temperature had fallen sufficiently to prevent spurting. The melt dissolved to a dark red water and after being heated for one half hour at 150°-200° potassium hydrate was added until the red color changed to yellow. A small portion of the melt was taken out, dissolved in water and acidified with dilute hydrochloric acid. To this solution of sulphuric dioxide was added, but no sulphur dioxide

Fig. 11 and 12.

Further action of Potassium Ethoxide on the Acetoacetatoacetoxyacetic Acid.

Some of the experiment above described was made on the ethyl ether of acetoacetatoacetoxyacetic acid. The corresponding acid group is very stable in this compound and it appears to be comparatively easy to replace it by hydroxyl. The question was then whether the stability in the experiment above described would be diminished sufficiently to permit ring formation. If ring formation does occur, and diketohexamethylene is formed, the change from the acetoacetic group to the acetonedicarboxylic group will be accompanied by the complete replacement

HCl	0.12	0.11	0.11
K.	0.13	0.13	0.13

Calcium Salt, $(C_6H_{11}O_7)_2Ca + 3H_2O$ — The salt was prepared by adding finely powdered calcium carbonate to a solution of the gluconic acid until the solution was neutral. The liquid was then evaporated to a syrup on the water bath and the residue dried in vacuo over sulphuric acid. The salt was then recrystallized from water and dried in vacuo over sulphuric acid.

0.2150 gram gave 0.1035 H_2O = 0.1150 gram H_2O; and 0.1665 gram gave 0.0800 H_2O = 0.0889 gram H_2O.

Boiling of Potassium Chloride with Potassium Hydroxide.

About 10 grams of potassium chloride were boiled with 10 c.c. of water and 10 grams of potassium hydroxide. About 5 grams of the potassium chloride were left undissolved. The addition of KOH is used in most commercial methods for the determination of potassium chloride by adding the solution slowly. The process was carried on for about 20 minutes, and during that time the liquid evaporated to dryness and the residue was then dissolved in water and acidified with hydrochloric acid. It was found that

Etc.

0.2410 gram of acid gave [illegible] gram $BaSO_4$ corresponding to [illegible] gram sulphur.

Calculated for

	$C_6H_3\begin{cases}COOH\\SO_2NH_2\\OH\end{cases}$	Found I	II	III	IV
C	38.71	—	—	—	38.44
H	3.22	—	—	—	3.40
N	6.45	6.56	6.63		—
S	14.75	—	—	14.83	—

Salts of Parahydroxymetasulphaminebenzoic acid.

Sodium Salt. $C_6H_3\begin{cases}COONa\\SO_2NH_2\\OH\end{cases} + 4H_2O$ — This salt was made by neutralizing a hot solution of the acid with sodium carbonate. The white radiating needles obtained are very soluble in water, but insoluble in boiling strong alcohol.

0.2963 gram of salt lost [illegible] gram

H_2O; and [illegible] [illegible] gram of the anhydrous [illegible] of [illegible].

	Calculated for $C_6H_3 \lt^{COOH}_{SO_3Na}_{CH_3} + 4H_2O$	Found
H_2O	23.15	23.?
Na	7.86	7.7?

Barium Salt, $(C_6H_3 \lt^{COO}_{SO_3}_{CH_3})Ba + 1\frac{1}{2} H_2O$. — The barium salt was made by neutralizing the hot aqueous solution of the free acid with freshly precipitated barium carbonate. It separated in small light [illegible] which are easily soluble in water and insoluble in boiling alcohol. 0.4387 gram of salt lost, at 120°, [illegible] gram H_2O and gave [illegible] gram barium sulphate.

	Calculated for $(C_6H_3 \lt^{COO}_{SO_3}_{CH_3})Ba + 1\frac{1}{2} H_2O$	Found
H_2O	7.13	6.52
Ba	36.01	36.21

Exp. 1. Nov 5

1. With potassium sulphate and sulphuric acid, the sulphate passes into the residue of the compound, leaving the inorganic part, with the sulphuric reaction taking place; the latter, however, to a very small extent.

2. With potassium chromate and sulphuric acid, but not sulphuric acid alone, after the compound, and the sulphuric acid gives a blue solution.

3. With potassium permanganate and sulphuric acid, with potassium hydroxide the result, potassium permanganate, no longer gives orthophosphoric acid.

4. With nitric acid, with potassium permanganate, potassium chromate, potassium hydroxide, potassium permanganate.